

High-temperature removal of cadmium from a gasification flue gas using solid sorbents

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Abstract

In this work, the retention capacity of solid sorbents for cadmium species present in coal gasification flue gases at high temperature was investigated. The influence of HCl(g) on the gas atmosphere was also evaluated. The study was carried out in a laboratory scale reactor, using synthetic gas mixtures with the sorbent as fixed bed. The sorbents tested were kaolin, limestone, alumina and fly ashes. The results obtained were compared with data from the works of other authors, who used similar solid sorbents in typical coal combustion flue gases. Whereas in the combustion atmospheres described in the literature, kaolin, limestone and alumina showed high retention capacities for cadmium compounds (0.5-40 mg g⁻¹), in the coal gasification atmospheres studied in the present work, the amount of cadmium captured by these solid sorbents was negligible. Fly ashes were found to be the most efficient for retaining cadmium in gasification atmospheres, their maximum retention capacity in the conditions studied being approx 0.75 mg g⁻¹.

Keywords: cadmium, hot gas cleaning, coal gasification

Introduction

The toxicity of cadmium, given its persistence in the environment and relatively rapid uptake and accumulation by living organisms makes this element a serious environmental risk. Cadmium is a species which may give rise to environmental problems not only in waste incineration processes, but also when emitted in lower concentrations during coal utilisation for energy production. As a trace element in coal, its concentration is generally lower than 3 ppm. In spite of this, the contribution of coal conversion processes to cadmium emissions to the environment cannot be ignored. The Convention on Long-range Transboundary Air Pollution was signed in 1979 and became effective in 1983. Since then, the Convention has

been expanded to include a number of agreements, among which is the 1998 protocol on Heavy Metals. The European Parliament passed a new directive on waste incineration (2000/76/EG) in line with the UN-ECE agreement.¹ This directive outlines the regulations and the emission limits for trace elements such as mercury, cadmium, lead and particulates and is applicable to waste incineration plants, cement kilns and coal fired boilers co-utilising bio-waste or waste derived fuels.

The development of new processes for coal based energy production, such as the Integrated Gasification Combined Cycle processes (IGCC), has made it necessary to devise new strategies to counteract trace element involvement in environmental problems that until recently was unknown. Although the behaviour of trace elements during conventional coal combustion processes is reasonably well known,²⁻⁴ there is a lack of similar knowledge for coal gasification systems. From studies already carried out, it can be inferred that cadmium compounds may be present in different proportions in the raw gases from coal gasification processes.²⁻⁸ It has been observed that cadmium volatility increases, as the C:O ratio diminishes and the gasification temperature rises.⁶ Moreover, the concentration of Cd in flue gases increases in gasifiers with particulate recycling.⁷ To compensate for the lack of experimental data, thermodynamic equilibrium studies using different computer programmes have been carried out. On the basis of these studies it has been concluded that much greater proportions of Cd will volatilise under atmospheric fluidised-bed gasification conditions than under fluidised bed combustion.^{4-5, 8}

The use of solid sorbents appears to be a promising technology for the removal of metal vapours from high temperature flue gases in gasification processes, and although emissions of cadmium from coal gasification can be expected to be low, it would be of interest to know if this element could be retained by the solid sorbents used to capture other corrosive or toxic species of major importance such as Na, As or Se.⁹⁻¹⁰ Selecting the right sorbent should take into account the capacity for retaining other species and also previous

experience with coal combustion and waste incineration processes.⁹⁻¹⁶ Various solid sorbents were investigated for cadmium retention in combustion atmospheres.¹¹⁻¹⁶ Silica, alumina, kaolin, emathlite and limestone have been used in a fixed bed at temperatures ranging between 700 and 800°C. Under these conditions, bauxite and kaolin have been observed to retain cadmium effectively.¹⁴ In a reactor simulating waste incineration, using sand, alumina, bauxite, zeolites and limestone, it has also been demonstrated that bauxite, zeolites and limestone are effective sorbents for cadmium capture. The retention mechanisms in these solid sorbents has been described as a complex combination of adsorption, condensation, diffusion and chemical reaction. It appears that, in a combustion environment, CdO $\text{Al}_2\text{O}_3(\text{s})$, $\text{CdSiO}_3(\text{s})$ and $\text{CdAl}_2\text{O}_4(\text{s})$, may be the products of chemical reactions between Cd compounds in gas phase and kaolin or bauxite.^{14,16}

The present study is part of a broader project in which the capture of different toxic trace elements in solid sorbents is evaluated.¹⁷⁻²⁰ The immediate aim of this work was to ascertain the influence of different coal gasification gas compositions on the capacity for cadmium retention by solid sorbents that had previously proved to have good characteristics for the retention of this element in coal combustion and waste incineration environments. The ultimate objective was to ascertain the possibility of simultaneous capture of cadmium using sorbents intended primarily for other toxic or corrosive compounds during IGCC.

Experimental section

Sorbents that have already been studied for trace element retention in combustion systems were evaluated in this work. Kaolin and limestone were taken from deposits located in Asturias (Spain), while fly ashes were collected from a fluidized bed power plant (La Pereda-Asturias) in which limestone is used in the bed. The sorbents were characterised by means of several techniques. X-ray Fluorescence (XRF) and Inductively Coupled Plasma-Mass (ICP-MS) were employed to determine the elemental composition. The crystalline species were

identified by X-ray Diffraction (XRD). The particle size was determined in a Coulter Counter apparatus, while the surface area was measured by volumetric adsorption of nitrogen at 77K. Theoretical studies based on thermodynamic equilibrium calculations were carried out in order to predict the cadmium species that would appear in gas phase and possible cadmium-sorbent reactions.

The experimental device used for the retention experiments consisted of a quartz reactor fitted to an internal and external tube and heated by two different furnaces (Figure 1). The trace element in gas phase was obtained from CdCl_2 evaporation at 638 °C. The sorbent and element source were placed inside the internal tube but heated separately in the two furnaces. Synthetic gas mixtures, typical of coal gasification processes, were passed through the reactor. Two gas mixtures were used: Mixture I, containing 57.6% CO , 3.30% CO_2 , 18.8% H_2 , 4% H_2O balanced with N_2 and Mixture II with the same composition plus 0.05% of HCl .

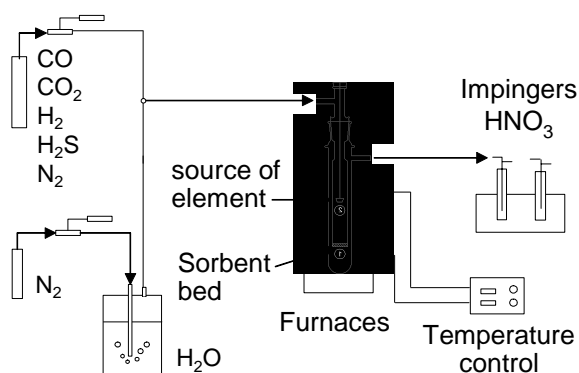


Figure 1. Schematic diagram of the experimental device.

These gas mixtures carried the element compound in vapour phase through the sorbent bed at a flow rate of 0.5 L min^{-1} . Any cadmium not retained in the sorbent was captured in impingers containing HNO_3 0.5N. The sorbent bed was prepared by mixing 1 g of sorbent with 3 g of sand. The resulting sorbent bed was 2.5 cm in diameter and 1.1 cm in height. In

order to avoid sorbent transformations due to the high temperatures used during the retention experiments, the solid sorbent was subjected to thermal treatment before the sorption experiments using the same gas composition at 900°C. The quantity of cadmium retained in the sorbent was analysed by ICP-MS after dissolution in a microwave oven. The sorption capacity (mg of cadmium per g of sorbent) and efficiency (percentage of cadmium retention) were evaluated. To determine maximum retention capacity (MRC), a series of experiments was conducted, in which the quantity of cadmium was gradually increased until the sorbent was saturated. Thermal stability studies of the post-retention sorbent were also carried out. Desorption was evaluated in a gasification atmosphere free of cadmium at the same temperature as for the retention experiment (750°C) for a period of three hours.

Results

The elemental composition of the sorbents is given in Table 1. The particle sizes were similar for all the sorbent samples used, i.e. 15-26 μm . Alumina had the highest surface area ($118 \text{ m}^2\text{g}^{-1}$), which was reduced to $83 \text{ m}^2\text{g}^{-1}$ after thermal treatment in the gasification atmospheres at 900°C. Similar values were measured for the original kaolin and fly ashes ($12 \text{ m}^2\text{g}^{-1}$), these values decreasing after thermal treatment to 2.5 and $3.5 \text{ m}^2\text{g}^{-1}$ respectively. The limestone surface before treatment was close to $5 \text{ m}^2\text{g}^{-1}$, increasing after thermal treatment to $10 \text{ m}^2\text{g}^{-1}$. XRD characterization of the sorbents, before and after thermal treatment, showed that kaolin underwent a dehydration process, whereas limestone was reduced to lime (CaO) in the atmosphere free of HCl (g). CaCl_2 was identified in the sorbent treated in the atmosphere containing HCl(g). Because the fly ashes were obtained at high temperatures, no transformations were to be expected during thermal treatment. However, reduction of CaSO_4 to CaS did occur. Alumina proved to be the most amorphous sorbent used in this work and accordingly no appreciable changes were observed by XRD.

Table 1. Elemental composition for the sorbents (%).

Compound	Kaolinite	Limestone	Fly ashes
Al ₂ O ₃	33.8	0.07	26.4
SiO ₂	50.6	0.53	48.1
CaO	0.04	99.6	6.47
MnO	0.01	0.01	0.05
MgO	0.06	0.31	1.54
Fe ₂ O ₃	0.83	0.04	6.75
K ₂ O	0.86	ND*	3.69
Na ₂ O	0.04	0.01	0.52
P ₂ O ₅	0.43	0.01	0.14
TiO ₂	1.11	0.01	0.96
S	0.05	ND	1.57
Cd ppm	0.97	1.73	1.00

*ND = not detected

Theoretical calculations using HSC chemistry software show that the equilibrium composition of the cadmium species depends on the temperature and gas atmosphere (Figure 2). In all cases Cd (g) is the dominant species at temperatures higher than 500°C, the temperature at which the experiments were carried out. CdCl₂(g) is formed at lower temperatures in the presence of HCl(g). Chemical reactions between the cadmium species and the sorbents could not be predicted from thermodynamic equilibrium data, the only exception being that of kaolin at temperatures lower than 550°C. In this case the gaseous cadmium species present in both atmospheres may theoretically react with cadmium to form CdSiO₃, (Figure 3).

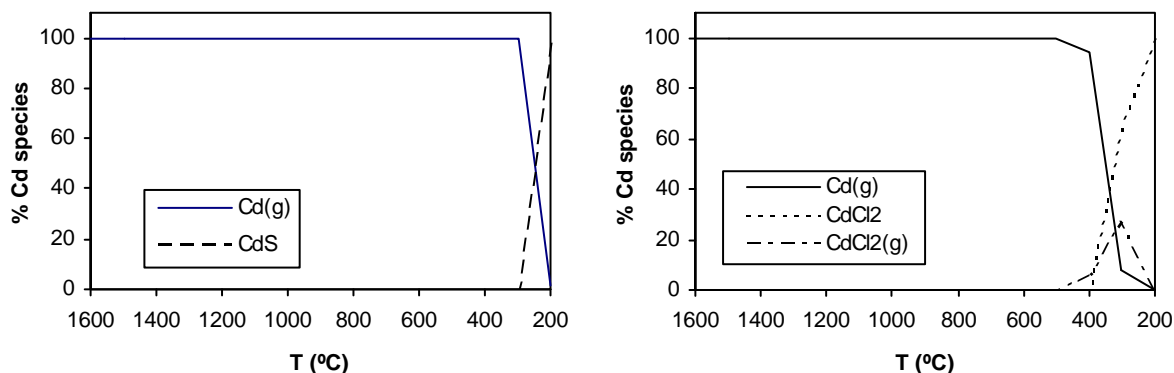


Figure 2. Equilibrium compositions for cadmium in (a) mixture I and (b) mixture II.

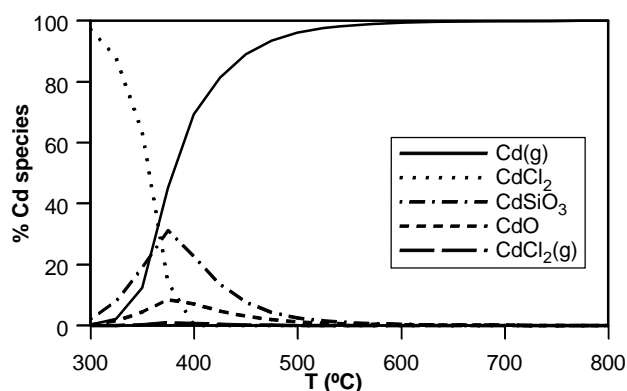


Figure 3. Equilibrium composition obtained for the Cd/Kaolinite system in both atmospheres.

The results obtained for the retention experiments are shown in Table 2. Retention capacities lower than $10 \mu\text{g g}^{-1}$ were obtained for all the sorbents, except for the fly ashes, for which values higher than $700 \mu\text{g g}^{-1}$ were reached. Maximum retention capacity may be considered to be similar in both atmospheres for all sorbents, again with the exception of the fly ash, in which MRC decreased from $750 \mu\text{g g}^{-1}$ to $280 \mu\text{g g}^{-1}$ in the presence of HCl (g) in the gasification atmosphere. It should also be noted that retention by limestone also increased slightly in the presence of HCl . In previous works carried out in combustion environments, cadmium was successfully captured in kaolin, with a degree of efficiency of around 90 %, and

Table 2. Maximum retention capacities (MRC, $\mu\text{g g}^{-1}$) and efficiencies (E, %) attained for cadmium retention using different solid sorbents, and the concentration retained after the desorption experiments in both atmospheres.

Sorbent	Mixture I			Mixture II		
	<i>E</i> %	<i>MRC</i> $\mu\text{g g}^{-1}$	<i>Retained</i> <i>after</i> <i>thermal</i> <i>treatment</i>	<i>E</i> %	<i>MRC</i> $\mu\text{g g}^{-1}$	<i>Retained</i> <i>after</i> <i>thermal</i> <i>treatment</i>
Kaolin	< 1	8.62 ± 0.26	1.74 ± 0.04	< 1	8.59 ± 0.55	1.67 ± 0.11
Limestone	<0.1	0.23 ± 0.05	*	<0.1	1.10 ± 0.21	*
Fly ash	10.5	746 ± 45.0	190 ± 20.0	4.48	280 ± 20.0	**
Alumina	<0.1	3.59 ± 0.28	0.22 ± 0.05	<0.1	3.27 ± 0.30	0.15 ± 0.03

*The thermal treatment was not carried out because the low concentration retained would lead to high uncertainties in the results

** The thermal treatment was not carried out because an increase in the time of the experiment implies decreasing retention

retention capacities between 0.5 to 5 mg g^{-1} .¹²⁻¹⁴ Moreover, 39 mg g^{-1} and 13 mg g^{-1} have been reported in other works,¹¹⁻¹⁶ with efficiencies close to 95% and between 8-80 % using alumina and lime respectively. Chemical reaction has been proposed by some researchers as the retention mechanism for cadmium in gas phase and alumina or aluminosilicates in combustion, whereas capture by hydrated lime has been described as a physical adsorption mechanism. However, the results obtained in the experiments carried out in this work in a gasification environment do not follow the same tendency. Efficiencies for kaolin limestone and alumina did not reach 1% and MRC was lower than 8 $\mu\text{g g}^{-1}$. The highest retentions were found in fly ashes where 10 % efficiency was obtained in a gas mixture free of HCl (g). Table 2 shows the amount of cadmium retained before and after thermal treatment. A notable loss of cadmium was observed after heating in the gasification atmosphere at 750°C for 3 hours, the amount of cadmium desorbed being similar in both atmospheres. The differences observed for

cadmium retention in solid sorbents in gasification atmospheres compared with the results in the literature for combustion are a consequence of the properties of the different species of cadmium present in both atmospheres. The reactions in combustion had been predicted and actually did occur for CdO(g) and $\text{Cd(OH)}_2\text{(g)}$ though the reactivity was lower if $\text{CdCl}_2\text{(g)}$ was the targeted species.¹¹ However the results were different in gasification atmospheres where Cd(g) was the species expected in the gas phase and where the formation of $\text{CdCl}_2\text{(g)}$ in the presence of HCl(g) was negligible. This behaviour in agreement with the assumption that cadmium would occur as Cd(g) in the gasification atmosphere of these experiments.

Although the thermodynamic data at equilibrium might lead one to expect the formation of a solid compound through a reaction between cadmium and kaolin, the low MRC obtained suggests this reaction may be limited by kinetics. Moreover, the loss of part of the retained element during thermal treatment points to a reversible adsorption mechanism. A similar behaviour was observed for cadmium retention in alumina, pointing in this case to physisorption. In previous works carried out in combustion atmospheres¹¹ the mechanism for the retention of cadmium in limestone could not be demonstrated. In a combustion atmosphere it has been observed that cadmium retention in limestone increases in the presence of HCl(g) as in the case of the gasification atmospheres of the present study. The increase in the retention capacity of limestone when HCl(g) is present in the gas atmosphere suggests that in the case of this sorbent, chlorine is involved in the retention mechanism as has been previously observed for combustion.

The highest retention was exhibited by the fly ashes, a sorbent with one of the lowest surface areas. This retention is even higher in an atmosphere free of HCl(g) . The Cd retained is partially desorbed by thermal treatment. According to thermodynamic data at equilibrium chemical reactions between fly ash components and Cd(g) cannot occur and possible reactions between cadmium and fly ash components require this element to be present as

Cd^{2+} . In this case, the sulphur species present on the surface of the fly ashes would lead to the formation of CdS . This could only be possible, however, if Cd(g) were oxidised on the fly ash surface, because as already deduced from thermodynamic calculations confirmed by retention data for kaolin and alumina, Cd was present as Cd(g) in the gasification atmosphere. Speculation that Cd(g) would oxidise on the fly ash surface is based on a similar behaviour found for mercury retention by fly ashes in which oxidation is attributed to the presence, among other factors, of Fe compounds.²¹⁻²² The lower MRC obtained when the gas mixture contained HCl(g) , and the fact that, in the presence of HCl(g) , retention decreases with time could be attributed to possible competition between Cl and S [5]. This would imply that CaS reacts with the Cl, and S is emitted from the sorbent, leading to a decrease in the number of active sites available for cadmium retention.



Conclusions

The results of this study show that the retention capacities of kaolin, limestone and alumina for cadmium in gasification flue gases are much lower than those reported in the literature for combustion atmospheres. However, fly ash, which is an industrial waste available in large amounts, is able to capture cadmium species in gasification atmospheres in high proportions. The capture mechanisms of cadmium species in fly ashes have not been dealt with in this work, as a more detailed study is necessary to ascertain whether the oxidation of cadmium on the surface of fly ashes is possible.

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